

A process for copolymerizing polar and non-polar monomers

The invention provides a process for copolymerising polar and non-polar monomers, a catalyst system suitable for this containing one or more transition metal compounds from groups 5-10 of the Periodic System, one or more radical-producers and optionally one or more co-catalysts, the polymers obtainable therefrom and use of the polymers which can be prepared by the process to produce molded articles of all types.

The copolymerisation of polar and non-polar monomers by radical polymerisation under high pressure is a known process. By way of example, the preparation of ethylene/acrylate copolymers may be mentioned (M. Buback et al., Macromol. Chem. Phys. 1997, 198, 3627) which proceeds at pressures between 1500 and 2500 bar between 130 and 225°C. Furthermore, ethylene/vinyl acetate copolymers are typically prepared at 2380 bar and 280°C. This high pressure of generally 500 to 3000 bar involves not only technical problems but also economic problems. The manufacture of ethylene/vinyl acetate/CO terpolymers also proceeds in a similar manner. Furthermore, the following may be mentioned here as examples: US 3 264 275, US 3 509 115, US 3 948 850, US 4 217 431, US 4 260 722 and US 4 267 090. Solution polymerizations of ethylene and vinyl acetate are described, for example, in EP-A-374 666, EP-A-341 499 and EP-A-307 755. Further references may be found in M. Busch et al., Macromol. Theory Simul. 1998, 7, 435.

According to the prior art, therefore, only acrylates or their salts, vinyl esters and carbon monoxide are suitable for use as monomers for the manufacture of ethylene copolymers. These are used in high pressure processes or else emulsion polymerisations with radical initiation.

Ethylene/acrylonitrile copolymers have hitherto only been accessible by subsequent hydrogenation of butadiene/acrylonitrile copolymers as described, for example, in DE-A-33 29 974.

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5 The alternating radical copolymerization of acrylic derivatives and ethene at low pressure is known and is described, for example, in DE-A-19 49 370 and in DE-A-44 04 320. The disadvantage of the process described is that copolymerization takes place only in the presence of equimolar, with respect to the polar monomers, amounts of acids or complexing agents and leads only to alternating products and that the removal of these complexing agents after completion of polymerization is achieved only by costly means.

10 WO-A-96/23010 discloses that acrylic ester derivatives or methyl vinyl ketone can be successfully copolymerized using diazadienepalladium complexes. The disadvantages of this process are that polar monomers are incorporated to only a small extent, that the molecular weight of the copolymers obtained is comparatively low even with low rates of incorporation and that comparatively high amounts of catalyst
15 have to be used to prepare the copolymers, which is a problem from an economic point of view.

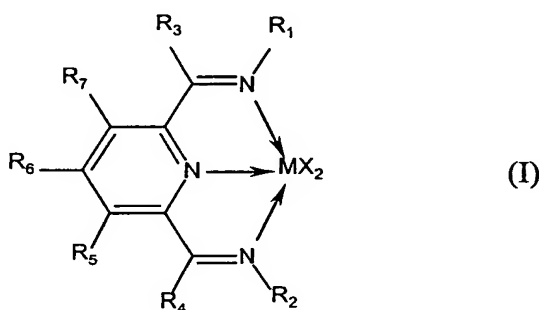
EP-A-558 143 describes a catalyst based on nickel which can be used to copolymerize ethylene and methyl methacrylate. The disadvantage of this process, however, is
20 that again only insufficient amounts of the polar comonomer are incorporated.

WO-A-98/27124 describes a process for polymerizing non-polar monomers (ethylene) using bisiminopyridyl cobalt or iron complexes of the general formula (I) and co-catalysts, and also the support of this type of catalyst systems in the liquid phase
25 or in a fluidised bed process. WO-A-98/30612 describes a process for polymerizing non-polar monomers (propylene) using the catalysts disclosed in WO-A-98/27124. WO-A-99/02472 describes bisiminopyridyl complexes of iron and a process for the oligomerisation and polymerization of ethylene.

30 WO-A-99/12981 describes a catalyst system consisting of bisiminopyridyl complexes of iron, cobalt, ruthenium or manganese for the homopolymerisation and co-

polymerization of ethylene and α -olefins and claims the use of ethene, propene, butene, hexene, methyl methacrylate, methyl acrylate, butyl acrylate, acrylonitrile, vinyl acetate and styrene. The disadvantage of the process described is that organoaluminium compounds have to be used to activate the bisiminopyridyl complexes and these, as is understood by any person skilled in the art, can react with the claimed polar monomers and thus are then no longer available for activating the catalyst.

G.J.P. Pritovsek et al., Chem. Commun. 1998, 849 describes bisiminopyridyl complexes of iron and cobalt of the general formula (I) and also their use as polymerization catalysts for non-polar monomers.



B.L. Small, M. Brookhart, A.M.A. Bennett, J. Am. Chem. Soc. 1998, 120, 4049 and B.L. Small, M. Brookhart, J. Am. Chem. Soc. 1998, 120, 7143 also describe bisiminopyridyl complexes of iron and cobalt of the general formula (I) and their use as polymerization catalysts. Bisiminopyridyl complexes of iron and cobalt of the general formula (I) and their use as polymerization catalysts for propylene are also described in C. Pellecchia, M. Mazzeo, D. Pappalardo, Macromol. Rapid. Commun., 19, 651-55 (1998) and B.L. Small, M. Brookhart, Macromolecules 1999, 32, 2120-30 (1999).

It is a common feature of all the documents that the polymerisations described there are purely coordinative polymerisations and copolymerization with polar molecules does not take place.

There is therefore the object of providing a process for the copolymerization of polar and non-polar monomers and a catalyst system suitable for this purpose.

5 Furthermore, there is the object of avoiding the disadvantages of the copolymerization processes described in the prior art.

Thus, the invention provides a process for copolymerizing polar and non-polar monomers, characterized in that at least one polar and at least one non-polar monomer are polymerized in the presence of one or more transition metal compounds from
10 groups 5-10 of the Periodic System according to the IUPAC 1985, one or more radical-producers and optionally one or more co-catalysts.

Polar monomers, in the context of the invention, are understood to be radically polymerizable monomers with more or less highly pronounced partial charge distribution within the molecule. Examples of these are chloroprene, styrene, acrylonitrile,
15 vinyl chloride, acrylic acid, acrylates, cyanacrylates, methacrylic acid, methacrylates, acrylamide, methacrylonitrile, vinyl acetate, propene oxide, ethene oxide, vinyl carbazole, vinylpyrrolidone, vinyl esters, and compounds built up from these parent molecules. Acrylonitrile, acrylates, methacrylates and styrene are preferred.

20 Non-polar monomers, in the context of the invention, are understood to be monomers which are polymerizable by coordinative polymerization, without any particular charge separation within the molecule. Examples of these are olefins, in particular ethylene, propylene, butenes, pentenes, hexenes, heptenes, octenes and their higher
25 homologues, diolefins, in particular butadiene, isoprene, pentadienes, hexadienes, heptadienes, octadienes, methyloctadienes, ethylidene norbornene, vinyl norbornene, norbornadienes, cyclooctadienes and their higher homologues and trienes.

Obviously the list of suitable polar and non-polar monomers could be extended, but a
30 longer list would certainly not contribute further to understanding the invention.

Suitable transition metal compounds, in the context of the invention, are compounds which correspond to the general formula (II),



5

wherein M is a metal from groups 5-10 of the Periodic System according to the IUPAC 1985, preferably a metal selected from the group comprising vanadium, chromium, manganese, iron, cobalt, nickel, ruthenium, rhodium and palladium,

10 wherein L is a 2-, 3- or 4-dentate chelating ligand, preferably a 3-dentate chelating ligand,

wherein Q is a mono-anionic or non-ionic ligand,

15 wherein a and b are each integers with $b \geq 1$, preferably $b \geq 2$ and a is calculated from the (total number of receptor coordination sites on M - b) / the number of donor coordination sites on the ligand.

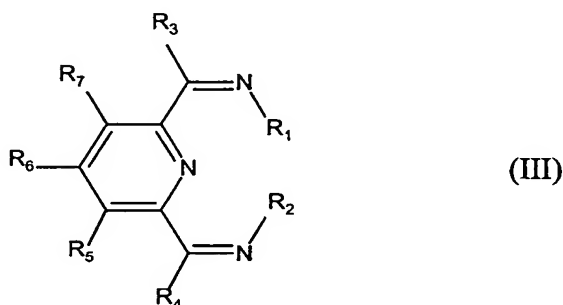
20 Examples of 2-dentate chelating ligands are diamines such as, for example, ethylene diamine, propylene diamine and butylene diamine, diimines, dipyridyls, dioximes, dioximates, 1,3-diketones such as, for example, acetylacetonate and hexafluoroacetylacetonate, carboxylates, diquinones, semiquinones, bisoxazolines, bithiazolines, 1,10-phenanthroline, 1,8-naphthyridine, pyridyl-2-alkylamines, pyridyl-2-dialkylamines, pyridyl-2-arylamine, pyridyl-2-diarylamine, 2-pyridylimines, pyridine-2-nitriles, dinitriles such as, for example, 1,2-benzodinitrile, 1,8-naphthodinitrile, sulfur diimines, dipyrazolyl borates, dipyrazolyl alkanes, dipyrazolyl ketones, aliphatic and aromatic diphosphines, phosphorimines or phosphorylides.

25 Preferred 2-dentate chelating ligands are ethylene diamine, propylene diamine, bipyridyl, diimines, 2-pyridylamines, 2-pyridylimines, ethylene diphosphine, 1,3-diphosphinopropane and phosphorylide ligands.

30

Examples of 3-dentate chelating ligands are terpyridine, triamines, 2,6-diaminopyridyls, 2,6-bisiminopyridyls, 2,6-biscyclopentadienylpyridines, bis-(2,6-hydrazonyl)-pyridines, trispyrazolyl borates, trispyrazolyl alkanes, trispyrazolyl ketones or triphosphines.

Preferred 3-dentate chelating ligands are triamines, trispyrazolyl borates, 2,6-diaminopyridyls, triphosphines and bisiminopyridyl ligands of the general formula (III)



wherein

R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 are chosen, independently, from hydrogen, optionally substituted C_1 - C_{10} -alkyl groups, optionally substituted C_6 - C_{14} -aryl groups or are part of a ring system.

Particularly preferably, R^1 and R^2 , independently, represent an optionally substituted aryl group and

R^3 , R^4 , R^5 , R^6 and R^7 are chosen, independently, from hydrogen, optionally substituted C_1 - C_{10} -alkyl groups, optionally substituted C_6 - C_{14} -aryl groups or are part of a ring system.

Examples of 4-dentate chelating ligands are tetraamines, tetrapyridines, tetraphosphines, salen, bis-(pyridylimino)-isoindolines and porphyrins.

Preferred 4-dentate chelating ligands are trialkyltetraamines, triaryltetraamines, tetraphosphines and salen.

In general, a list of different 2-, 3- or 4-dentate ligands may be found, for example, in G. Wilkinson, R.D. Gillard and J.A. McCleverty (eds), Comprehensive Coordination Chemistry - The synthesis, reaction, properties & applications of coordination compounds, Volume 2: Ligands, Pergamon Press, New York, 1st edition 1987, p. 30-56.

Examples of mono-ionic and non-ionic ligands Q are halide, hydride, C_1 - C_{10} -alkyl or -alkenyl, C_6 - C_{10} -cycloalkyl, C_6 - C_{14} -aryl, alkylaryl with a C_1 - C_{10} -grouping in the alkyl group and a C_6 - C_{14} -grouping in the aryl group, $-OR^8$, OR^8R^9 , $-NR^{10}R^{11}$, $-NR^{10}R^{11}R^{12}$, $-N(SiR^{10}R^{11}R^{12})_2$, $-N(SiR^{10}R^{11}R^{12})_3$, $-PR^{10}R^{11}$, $PR^{10}R^{11}R^{12}$, CO, tetrahydrofuran, pyridine, acetonitrile, wherein the Q's may be identical or different, wherein one or more of the two Q groupings may also be bridged and wherein R^8 to R^{12} may be chosen from H, C_1 - C_{10} -alkyl, C_3 - C_{10} -cycloalkyl, C_6 - C_{14} -aryl, alkylaryl or arylalkyl and may be identical or different.

A halogen is understood, by a person skilled in the art, to be fluorine, chlorine, bromine or iodine, preferably chlorine and bromine.

C_1 - C_{10} -alkyl groups are understood to be all linear or branched alkyl groups with 1 to 10 carbon atoms which are known to a person skilled in the art, such as methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, t-butyl, n-pentyl, i-pentyl, neo-pentyl and hexyl, heptyl, octyl, nonyl and decyl which, for their part, may also be substituted. Suitable substituents here are halogen, nitro, hydroxyl or also a C_1 - C_{10} -alkyl, and C_6 - C_{14} -cycloalkyl or aryl group, such as benzoyl, trimethylphenyl, ethylphenyl, chloromethyl, chloroethyl and nitromethyl.

C_6 - C_{14} -cycloalkyl groups are understood to be all mononuclear or polynuclear cycloalkyl groups with 6 to 14 carbon atoms which are known to a person skilled in the art, such as cyclohexyl, cycloheptyl, cyclooctyl and cyclononyl or also partly or fully

hydrogenated fluorenyl which, for their part, may also be substituted. Suitable substituents here are halogen, nitro, C₁-C₁₀-alkoxy or also C₁-C₁₀-alkyl and C₆-C₁₂-cycloalkyl or aryl groups such as methylcyclohexyl, chlorocyclohexyl and nitrocyclohexyl.

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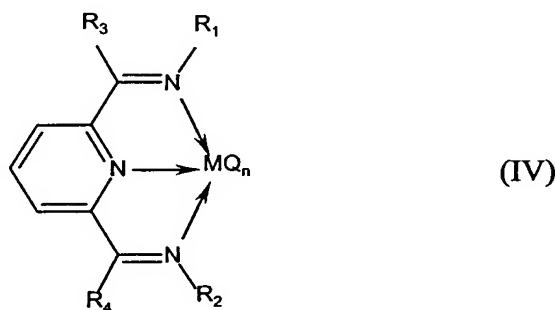
C₆-C₁₄-aryl groups are understood to be all mononuclear or polynuclear aryl groups with 6 to 14 carbon atoms which are known to a person skilled in the art, such as phenyl, naphthyl, fluorenyl which, for their part, may also be substituted. Suitable substituents here are halogen, nitro, C₁-C₁₀-alkoxy or also C₁-C₁₀-alkyl and C₆-C₁₄-cycloalkyl or -aryl groups such as bromophenyl, chlorophenyl, toluyl and nitrophenyl.

10

Q is preferably chosen from halide, in particular chloride and bromide, hydride, methyl, ethyl, butyl, tetrahydrofuran, CO and pyridine.

15

A particularly preferred transition metal compound is represented by the general formula (IV)



20 wherein

M is chosen from iron, cobalt, nickel or palladium,

Q is a mono-anionic or non-ionic ligand, in particular chlorine, methyl, ethyl or hydride,

25

R^1 and R^2 , independently, represent an optionally substituted aryl group, in particular a dialkylphenyl,

5 R^3 and R^4 are chosen, independently, from hydrogen, an optionally substituted C_1 - C_{10} -alkyl group, an optionally substituted C_6 - C_{14} -aryl group or are part of a ring system,

n is 1,2 or 3, in particular 2.

10 The transition metal compound is preferably selected so that the transition metal compound, optionally in the presence of a co-catalyst, can reversibly form a complex with the radically growing polymer chain and non-polar monomers, in particular olefins, can be inserted into the bond formed between transition metal and polymer chain. Without wishing to be firmly committed to this, the applicant's hypothesis is
15 that this insertion takes place via the so-called monometallic mechanism according to Arlman and Coissee in: Journal of Catalysis 1964, 3, 99 et seq. or the bimetallic mechanism according to Patat and Sinn in: Angewandte Chemie 1958, 70, 496.

Suitable radical-producers are all radical-producers known to a person skilled in the
20 art which initiate the radical polymerization of polar monomers and simultaneously do not react in a detrimental fashion with the transition metal compound.

Depending on the monomer combination used, the most suitable radical-producer can be chosen from the many radical-producers available by means of a few preliminary
25 trials. To list all of these would not contribute anything further to the understanding of the invention. A review of radical-producers which are suitable in principle can be found in G. Allen, J.C. Bevington (eds), Comprehensive Polymer Science, Pergamon Press, 1989, 123 et seq., to which express reference is made at this point.

30 Nevertheless, the following examples of suitable radical-producers may be explicitly mentioned: peroxides such as potassium or sodium peroxodisulfate, dibenzoyl per-

oxide, dicumyl peroxide, tert.-butylcumyl peroxide, cumyl hydroperoxide, tert.-butyl hydroperoxide, di-tert.-butyl peroxide, diisobutyryl peroxide, dilauryl peroxide, didecanoyle peroxide, diisopropyl peroxydicarbonate, dibutyl peroxydicarbonate, tert.-butyl peroxyisopropylcarbonate, tert.-butyl peroxy-pivalate, tert.-amyl peroxy-pivalate, tert.-butyl peroxyisononate, tert.-butyl peroxydiethylacetate or tert.-butyl peroxyacetate and diazo compounds such as 2,2'-azo-bis-(isobutyronitrile), 2,2'-azo-bis-(2-valeronitrile), 1,1'-azo-bis-(1-cyclohexanenitrile) or 4,4'-azo-bis-(4-cyanovale-
5 leric acid), or mixtures of these.

- 10 The choice of suitable radical-producer depends on the reaction medium and polymerization temperature. To summarize, it may once again be stressed that the radical-producer is chosen so that it initiates radical polymerization of the polar monomer under the given conditions (temperature, pressure, type of monomer, any solvent present, etc.) and at the same time does not react in a detrimental fashion with the
15 transition metal compound or the active transition metal species formed therefrom. For this reason molecular oxygen, for example, is not generally suitable as a radical-producer.

- 20 In the case of strongly coordinating ligands Q, such as halogen or hydride or even alkylene, it may be necessary to use a co-catalyst in order to replace ligands Q in the transition metal compound with so-called non-coordinating or weakly coordinating ligands. Express reference is made at this point to W. Beck et al., Chemical Reviews 1988, 88, 1405 and S. Strauss, Chemical reviews 1993, 93, 927.

- 25 In this case, coordination complex compounds may be used as co-catalysts, these being chosen from the group comprising strong, neutral Lewis acids, ionic compounds with Lewis acid cations or Broenstedt acid cations and non-coordinating anions.

- 30 Strong, neutral Lewis acids which can form stable salts of coordination complexes with Q are preferably compounds of the general formula V in which

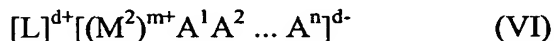


5 M^2 represents an element from group 3 of the periodic table of elements (IUPAC 1985), preferably B, Al or Ga, in particular B,

10 X^1 , X^2 and X^3 represent H, a C_1 - C_{10} -alkyl, C_6 - C_{14} -cycloalkyl, C_6 - C_{14} -aryl group or an alkylaryl, arylalkyl, halogenoalkyl, halogenoaryl, halogenoalkylaryl or halogenoarylalkyl group, each containing C_1 - C_{10} -alkyl, C_6 - C_{14} -cycloalkyl and C_6 - C_{14} -aryl groups and/or fluorine, chlorine, bromine or iodine, in particular halogenoaryl compounds, preferably perfluoro-substituted.

15 In the context of the invention, however, compounds of the general formula (V) in which X^1 , X^2 and X^3 are identical and preferably represent tris-(pentafluorophenyl) borane are particularly preferably used. These compounds and processes for preparing them are known per se and are described, inter alia, in WO-A-93/03067.

20 Compounds of the general formula VI are suitable as ionic compounds with Lewis or Brønstedt acid cations and non-coordinating anions,



wherein

25 L represents a Lewis acid cation in accordance with the Lewis acid/base theory, preferably carbonium, oxonium and/or sulfonium cations and also cationic transition metal complexes, in particular a triphenylmethyl cation, silver cation or ferrocenyl cation, or L represents a Brønstedt acid cation in accordance with the Brønstedt acid/base theory, preferably trialkylammonium, di-
30 alkylaryl ammonium and/or alkyl diaryl ammonium, in particular N,N-dimethylanilinium,

M^2 represents an element from group 3 of the periodic table of the elements (IUPAC 1985), in particular B, Al or Ga, preferably B,

5 A^1 to A^n represent singly negatively charged groups such as hydride, a C_1 - C_{28} -alkyl, C_3 - C_{14} -cycloalkyl, C_6 - C_{14} -aryl group or an alkylaryl, arylalkyl, halogenoalkyl, halogenoaryl, halogenoalkylaryl or halogenoarylalkyl group, each containing a C_1 - C_{28} -alkyl, C_7 - C_{14} -cycloalkyl and C_6 - C_{14} -aryl groups, or a halogen, alkoxide, aryl oxide or organometalloid group, and A_1 to A_n are
10 identical or different,

d is an integer from 1 to 6 and $d = n - m$,

n is an integer from 2 to 8 and

15

m is an integer from 1 to 6.

20

Preferred anions $[(M^2)^{m+} A^1 A^2 \dots A^n]^{d-}$ in the general formula VI are those in which A^1 to A^n are identical, spatially voluminous, aromatic hydrocarbon groups and M^2 is boron or aluminium, in particular tetraphenyl borate, tetrakis-(3,5-bis-(trifluoromethyl)phenyl) borate and tetrakis-(pentafluorophenyl) borate.

25

Obviously, mixtures of different compounds of the general formulae (II), (III), (IV), (V) and (VI) and mixtures of different radical-producers and different co-catalysts may also be used.

30

The radical-producer(s) are generally used at (total) concentrations in the range 0.01 mol.% to 5 mol.%, with respect to the total concentration of polar monomer(s), preferably in the range 0.01 - 1 mol.%. The most appropriate concentration can easily be determined in a few preliminary trials.

The transition metal compound(s) are used in the range 0.005 to 10 mol.%, with respect to the total concentration of radical-producer(s), preferably in the range 0.01 to 0.1 mol.%. The most appropriate concentration can easily be determined in a few preliminary trials.

5

The amount of co-catalyst(s) used depends on the number of ligands Q to be removed from the transition metal compound. Theoretically, one to 1.2 co-catalyst molecules are used per strongly coordinating ligand Q to be removed. This means that, in general, an amount in the range 0.01 to 20 mol.%, with respect to the total concentration of radical-producer(s), preferably in the range 0.01 - 0.5 mol.%, is used.

10

It may be advantageous to apply the catalyst system according to the invention to a support. In this case, bonding should preferably take place via the ligand L so that the components in the catalyst system do not react or interact in a detrimental fashion with the support.

15

Particulate organic or inorganic solids, the pore volumes in which are between 0.1 and 15 ml/g, preferably between 0.25 and 5 ml/g, the specific surface areas of which are greater than 1, preferably 10 to 1000 m²/g (BET), the particle sizes of which are between 10 and 2500 nm, preferably between 50 and 1000 nm, and the surface areas of which can be modified in an appropriate manner are preferably used as support materials.

20

The specific surface area is determined in a conventional manner using Brunauer, Emmet and Teller's method, J. Anorg. Chem. Soc. 1938, 60, 309, the pore volume is determined by McDaniels's centrifuge method, J. Colloid Interface Sci. 1980, 78, 31 and the particle size is determined by Cornillaut's method, Appl. Opt. 1972, 11, 265.

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The following may be mentioned as suitable inorganic solids without, however, intending to restrict the present invention: silica gels, precipitated silicas, clays, alumi-

nosilicates, talcum, zeolites, carbon blacks, inorganic oxides such as, for example, silicon dioxide, aluminium oxide, magnesium oxide, titanium dioxide, inorganic chlorides such as, for example, magnesium chloride, sodium chloride, lithium chloride, calcium chloride, zinc chloride or calcium carbonate. The inorganic solids mentioned which satisfy the specification mentioned above and are therefore particularly suitable for use as support materials are described in more detail, for example, in Ullmann's Enzyklopaedie der technischen Chemie, vol. 21, p. 439 et seq. (silica gels), vol. 23, p. 311 et seq. (clays), vol. 14, p. 633 et seq. (carbon blacks) and vol. 24, p. 575 et seq. (zeolites).

Powdered polymer materials, preferably in the form of a free-flowing powder, with the properties mentioned above, are suitable as organic solids. The following examples may be mentioned, without intending to restrict the present invention: polyolefins such as, for example, polyethene, polypropene, polystyrene, polystyrene-co-divinylbenzene, polybutadiene, polyethers such as, for example, polyethylene oxide, polyoxytetramethylene or polysulfides such as, for example, poly-p-phenylene sulfide. Particularly suitable materials are polypropylene, polystyrene or polystyrene-co-divinylbenzene. The organic solids mentioned, which comply with the specification mentioned above and are therefore particularly suitable for use as support materials are described in more detail, for example, in Ullmann's Enzyklopaedie der technischen Chemie, vol. 19, p. 195 et seq. (polypropylene) and vol. 19, p. 265 et seq. (polystyrene).

The supported catalyst system may be prepared over a wide temperature range. The process is usually performed at temperatures of -80 to +200°C, preferably -20 to 150°C, in particular 20 to 100°C.

The invention also provides a composition consisting of one or more transition metals from groups 5-10 of the Periodic System according to IUPAC 1985, one or more radical-producers and optionally one or more co-catalysts and its use as a catalyst system in a process for co-polymerization of polar and non-polar monomers.

Polymerization is preferably performed by placing the monomers in contact with the composition according to the invention dissolved in suitable solvents, in the gaseous or liquid phase, finely distributed or suspended in a liquid diluent.

- 5 Other gases or finely distributed liquids may be mixed with the gaseous, liquid or sprayed monomers, these being used for either diluting, spraying or dissipating heat.

10 Liquids or liquefied gases which are known to a person skilled in the art and do not have a detrimental effect on polymerization or the catalyst system, in particular saturated hydrocarbons such as pentane, hexane, cyclohexane, petrol and petroleum ether, are suitable as diluents or solvents.

15 Polymerization may be performed at pressures of 0.01 bar to 1000 bar, preferably 0.1 to 500 bar, in particular 1 to 100 bar, quite specifically 1 to 10 bar. In general, polymerization is performed at temperatures of -20 to 250°C, preferably 0 to 200°C, in particular 20 to 160°C. As a trivial point, the temperature has to be matched to the radical-producer being used, since the radical-producer also has to decompose at this temperature.

- 20 Since the transition metal compound is generally sensitive to oxygen and water, it is advantageous to exclude oxygen and water.

25 The sequence of mixing the individual constituents in the composition may be any order at all. As a rule, the final composition is placed in contact with the monomer mixture and then the temperature is increased to above the decomposition temperature of the radical-producer.

30 The invention also provides use of the polymers obtainable in accordance with the invention for preparing molded items of any type, in particular films, sheets, hoses, sections, sheathing, extrudates and injection molded articles. At the molecular level, said polymers are statistical copolymers and not AB-block copolymers. Another pre-

ferred use is use as a starting material for adhesives and additives, in particular oil additives. The composition may be varied over a wide range, depending on the conditions used, the catalytically active composition and the monomer composition and concentration. The molar fraction of polar monomers incorporated to non-polar monomers incorporated is generally in the range 0.05 - 0.95.

Polymers prepared according to the invention contain homopolymers of the individual monomers as impurities. For specific applications, it may be advantageous to remove these using appropriate methods, such as fractional precipitation or extraction processes.

The following examples are intended to explain the present invention in more detail without, however, restricting this to the examples.

Examples

5 All reactions were performed with the exclusion of air and moisture, if required, and using the variable high vacuum technique. The solvents used were dry, saturated with purified argon and stored under an argon atmosphere.

10 2,2'-azo-bis-(isobutyronitrile), AIBN, is commercially available (Merck KgaA, Germany) and was used without further purification. The potassium perfluorophenyl borate, $K[B(C_6F_5)_4]$, used was prepared from the corresponding lithium compound using S. Cohen and A. Massey's method, Adv. Fluor. Chem. 6, 83-285 (1970), $Na[B(C_6H_5)_4]$ was purchased from Merck KgaA, Germany and used without further purification.

15 The polymerization reactions were performed in a 1 l Buechi glass autoclave at 60°C and the amounts of ethene were determined using a mass flow-meter. The polymers were isolated by precipitating in ethanol, purified by washing with ethanol and dried under vacuum.

20 The concentration of ethene in the polymers was determined using NMR spectroscopy in d_6 -dimethylsulfoxide, the glass transition temperature T_g was determined by DSC and the weight average of the molecular weight M_w and polydispersity M_w/M_n were determined using GPC against a polystyrene standard in dimethylacetamide.

Synthesis of the complexes**2,6-dibenzoylpyridine-bis-(2,6-dimethylphenylimino)-cobalt dichloride
(complex A)****5 Example 1a:****Synthesis of 2,6-dibenzoylpyridine**

10 In a 500 ml round-bottomed flask with a reflux condenser, 32.4 g (243 mmol) of anhydrous aluminium trichloride are added to 20.0 g (98 mmol) of pyridine-2,6-dicarboxylic acid chloride in 250 ml of dry benzene under an Ar atmosphere. The mixture is stirred under reflux for 4 h, then cooled, stirred overnight at room temperature and then again stirred under reflux for 6 h. After cooling, the mixture is carefully poured into 500 ml of ice water. The organic phase is separated and the aqueous phase is washed twice, using 100 ml of diethyl ether each time. The combined organic phases
15 are washed twice, using 100 ml of water each time, and then dried over sodium sulfate. The solvents are removed on a rotary evaporator and the product is recrystallised from diethyl ether. Yield: 16.80 g.

20 ¹H NMR (in acetone-d₆/TMS): δ = 8.32-8.26 (m, 3H), 8.14-8.06 (m, 4H), 7.7-7.4 (m, 6H).

MS: 287, 259, 230, 182, 105, 77, 51

Example 1b**25 Synthesis of 2,6-dibenzoylpyridine-bis-(2,6-dimethylphenylimino)-nickel dibromide**

30 1.20 g (5.5 mmol) of anhydrous nickel dibromide are added to a solution of 1.42 g (5 mmol) of 2,6-dibenzoylpyridine and 1.2 ml (10 mmol) of 2,6-dimethylaniline in 50 ml of glacial acetic acid. The mixture is stirred under reflux for 6 h. An orange-

brown powder precipitates and this is filtered hot. The residue is washed twice, using 50 ml of diethyl ether each time, and dried. Yield: 3.35 g

FT-IR (KBr): $\nu(\text{C}=\text{N}) = 1579 \text{ cm}^{-1}, 1610 \text{ cm}^{-1}$.

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Example 1c

Synthesis of 2,6-dibenzoyl-bis-(2,6-dimethylphenylimino)-pyridine

10 ml of a 10 % strength aqueous NaCN solution are added to a suspension of 0.71 g (1 mmol) of 2,6-dibenzoylpyridine-bis-(2,6-dimethylphenylimino)-nickel dibromide in 10 ml of THF and stirred at RT for 30 min. The organic phase is separated and dried over sodium sulfate. After removing the solvent, the bis-iminopyridyl derivative remains as a pale yellow powder. Yield: 0.40 g.

15 ^1H NMR (in CDCl_3): $\delta = 8.07$ (m, 1H), 7.77 (m, 2H), 7.43-7.36 (m, 6H), 6.93-6.81 (m, 10H), 2.01 (s, 12H); MS: $M^+ = 494 \text{ g/mol}$.

Example 1d

20 **Synthesis of 2,6-dibenzoylpyridine-bis-(2,6-dimethylphenylimino)-cobalt dichloride**

0.07 g (0.5 mmol) of anhydrous cobalt(II) chloride are added to a solution of 0.28 g (0.5 mmol) of 2,6-dibenzoyl-bis-(2,6-dimethylphenylimino)-pyridine in 20 ml of dry THF, at room temperature, and the mixture is stirred at room temperature for 48 hours. Then the solution is evaporated down to one half the volume and 100 ml of hexane is added thereto. The bisiminopyridylcobalt complex precipitates as a pale brown powder and is dried under vacuum after filtration. Yield: 0.15 g.

FT-IR (KBr): $\nu(\text{C}=\text{N}) 1571 \text{ cm}^{-1}$.

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**2,6-dibenzoylpyridine-bis-(2,6-diisopropylphenylimino)-cobalt dichloride
(complex B)**

Example 2a

5 Synthesis of 2,6-dibenzoyl-bis-(2,6-diisopropylphenylimino)-pyridine

10 A solution of 0.4 ml (3.5 mmol) of titanium tetrachloride in 20 ml of toluene is added dropwise to a solution of 3.6 ml (19 mmol) of 2,6-diisopropylaniline and 0.91 g (3.2 mmol) of 2,6-dibenzoylpyridine, which had been prepared in the same way as described in the example for preparing complex A, in 50 ml of toluene at 0°C. After completion of the addition procedure, the mixture is stirred at room temperature for 90 min and then under reflux for 12 h. After cooling to room temperature, the orange suspension is filtered and the residue is washed three times, using 30 ml of toluene each time. The solvent is distilled off and 100 ml of hexane are added to complete
15 precipitation of the hydrochloride. The mixture is filtered again and the residue is washed free of solvent. Then the residue is recrystallised from methanol. At -18°C, 2,6-dibenzoyl-bis-(2,6-diisopropylphenylimino)-pyridine crystallizes out as a pale yellow solid. Yield: 0.92 g.

20 ¹H NMR (in CDCl₃): d = 8.05-6.83 (m, 19H), 2.87 (m, 4H), 1.10-0.89 (dd, 24H).

Example 2b

**Synthesis of 2,6-dibenzoylpyridine-bis-(2,6-diisopropylphenylimino)-cobalt(II)
dichloride**

25 0.07 g (0.5 mmol) of anhydrous cobalt(II) chloride are added, at room temperature, to a solution of 0.30 g (0.5 mmol) of 2,6-dibenzoyl-bis-(2,6-diisopropylphenylimino)-pyridine in 30 ml of dry THF and the mixture is stirred at room temperature for 12 h. Then the solution is evaporated down to half the volume and 100 ml of hexane is
30 added thereto. The bisiminopyridylcobalt complex precipitates out as a golden yellow precipitate and is dried under vacuum after filtration. Yield: 0.26 g.

FT-IR (KBr): $\nu(\text{C}=\text{N})$ 1572 cm^{-1} .

Polymerization trials

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Example 3

Radical polymerization of acrylonitrile (comparison trial)

10 ml (150 mmol) of acrylonitrile in 200 ml of toluene are initially introduced into a
10 1000 ml glass autoclave. After adding 230 mg (1.4 mmol) of AIBN, the mixture is
heated to 65°C and stirred for 4 h at this temperature. Yield: 1.98 g.

Example 4

Polymerization of ethene/AN with [(2,6-iPr₂Ph)₂PhPyr]CoCl₂/K[B(C₆F₅)₄]/AIBN

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10 ml (150 mmol) of acrylonitrile in 200 ml of toluene are initially introduced into a
1000 ml glass autoclave. Then 246 mg (1.5 mmol) of AIBN, 11 mg (1.5×10^{-2}
mmol) of cobalt compound B and 24 mg (3×10^{-2} mmol) of K[B(C₆F₅)₄] are added,
one after the other. The reactor is sealed and ethene is introduced until the pressure
reaches 4 bar, so that the molar ratio of acrylonitrile to ethene is 2:1. Then the mix-
20 ture is heated to 65°C and polymerized for 4 h at this temperature. Yield: 1.17 g.

Example 5

Polymerization of ethene/AN with [(2,6-iPr₂Ph)₂PhPyr]CoCl₂/K[B(C₆F₅)₄]/AIBN

25

5 mg (3×10^{-2} mmol) of AIBN and 10 ml (150 mmol) of acrylonitrile in 200 ml of
toluene are initially introduced and heated to 60°C. Then 22 mg (3×10^{-2} mmol) of
cobalt complex B and 47.4 mg (6×10^{-2} mmol) of K[B(C₆F₅)₄] are added. The
reactor is sealed and ethene is introduced until the pressure reaches 4 bar, so that the
30 molar ratio AN:E = 2:1, heated to 65°C and polymerized at this temperature for 24 h.
Yield: 0.35 g.

Example 6**Polymerization of ethene/AN with [(2,6-*i*Pr₂Ph)₂PhPyr]CoCl₂/K[B(C₆F₅)₄]/AIBN**

- 5 5 ml (75 mmol) of acrylonitrile in 200 ml of toluene are initially introduced. Then
244 mg (1.5 mmol) of AIBN, 11 mg (1.5×10^{-2} mmol) of cobalt complex B and
24 mg (3×10^{-2} mmol) of K[B(C₆F₅)₄] are added, one after the other, at 60°C. The
reactor is sealed and ethene is introduced until the pressure reaches 4 bar, so that the
molar ratio AN:E = 1:1, heated to 65°C and polymerized at 65°C for 4 h. Yield:
10 0.22 g.

Example 7**Polymerization of ethene/AN with [(2,6-Me₂Ph)₂PhPyr]CoCl₂/K[B(C₆F₅)₄]/AIBN**

- 15 10 ml (150 mmol) of acrylonitrile in 200 ml of toluene are initially introduced. Then
246 mg (1.5 mmol) of AIBN, 9.3 mg (1.5×10^{-2} mmol) of cobalt compound A and
24 mg (3×10^{-2} mmol) of K[B(C₆F₅)₄] are added, one after the other, at 60°C. The
reactor is sealed and ethene is introduced until the pressure reaches 4 bar, so that the
molar ratio AN:E = 2:1, heated to 65°C and polymerized at this temperature for 4 h.
20 Yield: 0.84 g.

Example 8**Polymerization of ethene/AN with [(2,6-Me₂Ph)₂PhPyr]CoCl₂/K[B(C₆F₅)₄]/AIBN**

- 25 5 ml (75 mmol) of acrylonitrile in 200 ml of toluene are initially introduced. Then
245 mg (1.5 mmol) of AIBN, 9.3 mg (1.5×10^{-2} mmol) of cobalt complex A and
24 mg (3×10^{-2} mmol) of K[B(C₆F₅)₄] are added, one after the other, at 60°C. The
reactor is sealed and ethene is introduced until the pressure reaches 4 bar, so that the
molar ratio AN:E = 1:1, heated to 65°C and polymerized at this temperature for 4 h.
30 Yield: 0.14 g.

Example 9**Polymerization of ethene/AN with**

- 5 10 ml (150 mmol) of acrylonitrile in 200 ml of toluene are initially introduced. Then
246 mg (1.5 mmol) of AIBN, 11 mg (1.5×10^{-2} mmol) of cobalt compound B and
11.3 mg (3×10^{-5} mmol) of $\text{Na}[\text{B}(\text{C}_6\text{H}_5)_4]$ are added, one after the other, at 60°C. The
reactor is sealed and ethene is introduced until the pressure reaches 4 bar, so that the
molar ratio AN:E = 2:1, heated to 65°C and polymerized at this temperature for 4 h.
10 Yield: 0.95 g

Example 10

- 15 10 ml (150 mmol) of acrylonitrile in 200 ml of toluene are initially introduced. Then
246 mg (1.5 mmol) of AIBN, 11 mg (1.5×10^{-2} mmol) of cobalt compound B and
24 mg (3×10^{-2} mmol) of $\text{K}[\text{B}(\text{C}_6\text{F}_5)_4]$ are added, one after the other, at 60°C. The
reactor is sealed and ethene is introduced until the pressure reaches 6 bar, so that the
molar ratio AN:E = 1.5:1, heated to 65°C and polymerized at this temperature for 4h.
20 Yield: 1.17 g

Example 11**Polymerization of ethene/styrene with**

- 25 5 ml (43 mmol) of styrene in 200 ml of toluene are initially introduced. Then 142 mg
(0.9 mmol) of AIBN, 6.3 mg (0.9×10^{-2} mmol) of cobalt compound B and 6 mg
(1.8×10^{-2} mmol) of $\text{Na}[\text{B}(\text{C}_6\text{H}_5)_4]$ are added, one after the other. The reactor is
sealed and ethene is introduced until the pressure reaches 2.6 bar, so that the molar
30 ratio styrene:E = 1:1, heated to 65°C and polymerized at this temperature for 4 h.
Yield: 0.19 g

Example 12**Polymerization of ethene/styrene with**

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5 ml (43 mmol) of styrene in 200 ml of toluene are initially introduced. Then 180 mg (1.1 mmol) of AIBN, 16 mg (2.2×10^{-2} mmol) of cobalt compound B and 17 mg (4.9×10^{-2} mmol) of $\text{Na}[\text{B}(\text{C}_6\text{H}_5)_4]$ are added, one after the other. The reactor is sealed and ethene is introduced until the pressure reaches 5.3 bar, so that the molar ratio styrene:E = 1:2, heated to 65°C and polymerized at this temperature for 4 h.

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Yield: 0.20 g

Example 13**Polymerization of ethene/MA with**

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10 ml (112 mmol) of methyl acrylate in 200 ml of toluene are initially introduced. Then 180 mg (1.1 mmol) of AIBN, 8 mg (1.1×10^{-2} mmol) of cobalt compound B and 8.6 mg (2.5×10^{-2} mmol) of $\text{Na}[\text{B}(\text{C}_6\text{H}_5)_4]$ are added, one after the other. The reactor is sealed and ethene is introduced until the pressure reaches 3.4 bar, so that the molar ratio MA:E = 2:1, heated to 65°C and polymerized at this temperature for 4 h. Yield: 4.10 g

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Example 14

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Polymerization of ethene/MA with

5 ml (56 mmol) of methyl acrylate in 200 ml of toluene are initially introduced. Then 180 mg (1.1 mmol) of AIBN, 8 mg (1.1×10^{-2} mmol) of cobalt compound B and 8.6 mg (2.5×10^{-2} mmol) of $\text{Na}[\text{B}(\text{C}_6\text{H}_5)_4]$ are added, one after the other. The reactor is sealed and ethene is introduced until the pressure reaches 3.4 bar, so that the molar

30

ratio MA:E = 1:1, heated to 65°C and polymerized at this temperature for 4 h. Yield: 1.77 g

Example 15

- 5 **Polymerization of ethene/MA with**
[(2,6-iPr₂Ph)₂PhPyr]CoCl₂/Na[B(C₆H₅)₄]/AIBN

10 5 ml (56 mmol) of methyl acrylate in 200 ml of toluene are initially introduced. Then 180 mg (1.1 mmol) of AIBN, 8 mg (1.1×10^{-2} mmol) of cobalt compound B and 8.6 mg (2.5×10^{-2} mmol) of Na[B(C₆H₅)₄] are added, one after the other. The reactor is sealed and ethene is introduced until the pressure reaches 5.1 bar, so that the molar ratio MA:E = 1:1.5, heated to 65°C and polymerized at this temperature for 4 h. Yield: 2.01 g

- 15 **Example 16**

Radical polymerization of methyl acrylate (comparison trial)

20 10 ml (112 mmol) of methyl acrylate in 200 ml of toluene are initially introduced into a 1000 ml glass autoclave. After adding 180 mg (1.1 mmol) of AIBN, the mixture is heated to 65°C and stirred at this temperature for 4 h. Yield: 4.72 g.

Overview of results of polymerization trials

Ex. No.	Complex		Borate		AIBN	t_{poly}	Ethene	AN	Styrene	MA	Yield	Ethene in polymer	M_w	M_w/M_n	T_g (2 nd Heat)
	A	B	K(pfb)	Na(phb)	[mmol]	[h]	[mmol]	[mmol]	[mmol]	[mmol]	[g]	[mol-%]	[g/mol]		[°C]
3	--	--	--	--	1,4	4	--	150	--	--	1,98	0	n.d.	n.d.	109
4	--	0,015	0,030	--	1,5	4	75	150	--	--	1,17	10,3	31370	2,00	87
5	--	0,015	0,030	--	0,03	24	75	150	--	--	0,35	n.d.	n.d.	n.d.	93
6	--	0,015	0,030	--	1,5	4	75	75	--	--	0,22	21,6	9900	1,81	58
7	0,015	--	0,030	--	1,5	4	75	150	--	--	0,84	9,1	21270	1,87	89
8	0,015	--	0,030	--	1,5	4	75	75	--	--	0,14	16,3	8820	1,43	67
9	--	0,015	--	0,030	1,5	4	75	150	--	--	0,95	9,7	23910	2,01	84
10	--	0,015	0,030	--	1,5	4	100	150	--	--	1,17	11,2	24510	1,96	80
11	--	0,009	--	0,018	0,9	4	43	--	43	--	0,19	n.d.	n.d.	n.d.	60
12	--	0,022	--	0,049	1,1	4	86	--	43	--	0,20	n.d.	n.d.	n.d.	58
13	--	0,011	--	0,025	1,1	4	56	--	--	112	4,10	n.d.	n.d.	n.d.	-1,5
14	--	0,011	--	0,025	1,1	4	56	--	--	56	1,77	n.d.	n.d.	n.d.	-3
15	--	0,011	--	0,025	1,1	4	84	--	--	56	2,01	n.d.	n.d.	n.d.	6
16	--	--	--	--	1,1	4	--	--	--	112	4,72	0	n.d.	n.d.	-1

Na(phb) = Na[B(C₆H₅)₄] and K(pfb) = K[B(C₆F₅)₄]; n.d. = not determined; t_{poly} = polymerization time; AIBN = azobisisobutyronitrile; AN = acrylonitrile;

MA = methyl acrylate; M_w determined via GPC in dimethylacetamide (DMAc) ref. to a poly styrene-standard.